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# ALLOY-BASED NANO-CRYSTAL TEXTURE AND METHOD OF PREPARING SAME

## Field of the Invention

The present invention relates to a nano-crystal texture and a method of preparing the same. More particularly, the present invention relates to a nano-crystal texture which improves ductility of a material and is useful for achievement of a material known as a super-metal, and method of preparing the same.

## Related Art

Reduction of the size of crystal grain has conventionally been tried in various manners as a method for improving strength and ductility of an alloy material. Materials having a high strength have so far been achieved by the use of the thus developed methods.

In spite of various contrivances made in the composition and heat treatment, however, further remarkable improvement of the strength level has been limited. With conventional techniques, it is difficult to largely improve strength to, for example, ten times as high. There is therefore a demand for quite new findings essentially different from the conventional technical knowledge.

The present invention has an object to overcome the conventional technical limits as described above, and to provide a novel practicable material permitting an epoch-making breakthrough and a simple method for preparing the same.

## Summary of the Invention

The present invention provides an alloy-based nano-crystal texture, wherein, in an alloy capable of forming an amorphous state, nano-scale crystals are present as a crystal texture as arranged in an identical orientation.

The invention provides also a method of preparing an alloy-based nano-crystal texture in which, in an alloy capable of forming an amorphous state, nano-scale crystals are present as a crystal texture as

arranged in an identical orientation, comprising the step of heating an amorphous alloy at a temperature lower than the crystallization temperature.

#### Brief Description of the Drawings

Fig. 1 is an ordinary electron micrograph of a crystal grain formed when annealing the material at 687 K for two hours;

Fig. 2 is an electron micrograph illustrating that one of the crystal grains shown in Fig. 1 is composed of nano-crystals of 20 to 40 nm;

Fig. 3 is a high-resolution electron micrograph when an electron beam is irradiated from the [111] bcc orientation to show a nano-crystal texture in an embodiment of the invention;

Fig. 4 is an enlarged electron micrograph of the box portion shown in Fig. 3;

Fig. 5 is a high-resolution electron micrograph when an electron beam is irradiated from the [001] bcc orientation to show the nano-crystal texture;

Fig. 6 is an enlarged electron micrograph of the box portion shown in Fig. 5;

Fig. 7 is a diagram illustrating the atomic arrangement of a precipitate produced on the interface between adjacent nano-crystals;

Fig. 8 is a schematic view illustrating the process of formation of a nano-crystal texture having an identical orientation, as viewed from the [001] bcc orientation;

Fig. 9 is a schematic view illustrating the process of formation of a nano-crystal texture having an identical orientation, as viewed from the [111] bcc orientation; and

Fig. 10 is a schematic view illustrating the process of formation of a nano-crystal texture having an identical orientation, showing the whole view three-dimensionally.

#### Detailed Description of the Invention

Now, the present invention will be described below further in

detail by means of embodiments. First, the nano-crystal texture of the invention has a unique structure in which as many as several tens of thousand nano-crystals having a nano-scale size, i.e., a size of an extra-fine diameter represented in units smaller than 100 nano-meter (nm), have an identical orientation in fine grains in the common meaning, for example, of a micron-meter ( $\mu\text{m}$ )-scale.

Such a nano-crystal texture has a composition deviated from the stoichiometric composition, and further, is characterized by falling under an alloy system capable of forming an amorphous state. When the composition deviates toward the side of easier production of precipitate, it is very difficult, upon transition from amorphous to crystalline state, to contain excessive atoms in the form of a uniform solid solution. Immediately upon crystallization, therefore, the crystallized portion becomes a regular ordered alloy having a stoichiometric composition, and excessive atoms of elements on the excessive component side are released into the amorphous phase. When this exceeds a certain amount, a thinplate-shaped precipitate is formed, while making boundaries, thus resulting in nano-crystals. A nano-crystal texture having an identical orientation is prepared by repeating this process.

More specifically, the composition of the alloy-based nano-crystal texture of the invention deviates toward the side of easier production of precipitate, preferably by about 1 to 5% from the stoichiometric composition. In a Ti-Ni alloy, for example, deviation toward Ti side (Ti excess side) is conceived. Such a deviation is appropriately determined from the phase diagram of the alloy. Applicable alloys include, for example, Ti-Ni alloys, Ti-Co alloys, Ti-Al alloys and Fe-Al alloys. The diameter of a nano-scale crystal is within a range of from about 10 to 60 nm, and the diameter of a crystal grain in the conventional sense is within a range of from about 1 to 10  $\mu\text{m}$ .

The nano-crystal texture of the invention is produced in the process of crystallization from an amorphous state. The alloy should therefore fall under an alloy system capable of achieving an amorphous

state. That is, for example, preparation of a nano-crystal texture of the invention can be prepared in Ti-Ni, Ti-Al, Ti-Co and Fe-Al alloy systems and alloy systems showing a phase diagram similar to those of these alloys, in which the amorphous states are capable to be produced.

Production of the nano-crystal texture of the invention is based on a mechanism in which a regular ordered lattice having a stoichiometric composition is formed simultaneously with crystallization, and excessive alloy elements are released as a precipitate into the interface between the nano-crystal grains and the amorphous phase. It is therefore necessary that the alloy system has a composition slightly deviated from the stoichiometric composition toward easier formation of a precipitate.

The formation thereof is made possible by heating the amorphous alloy at a temperature lower than the crystallization temperature.

The material provided by the invention is theoretically expected to have a yield strength about ten times as high even as compared with a material composed of an extra-fine grain size of 1 to 2  $\mu\text{m}$ , and about 30 times as high as compared with an ordinary crystal grain size of 20 to 40  $\mu\text{m}$ . In addition, the material of the invention, composed of nano-crystals with an identical orientation, can be extended by large amounts and is highly resistant to rupture.

Further, the method of the present invention is based on a subtle combination of the tendency toward ordering and the tendency of precipitation in the process of crystallization from the amorphous state. It is therefore very easy to industrialize only if an appropriate alloy system is available, and to achieve properties known as the super-metal.

Now, the present invention will be described further in detail below by means of examples.

### Examples

A nano-crystal having a diameter of from 20 to 40 nm was produced by heating a Ti-48.2 at% Ni alloy in the amorphous state, of which the composition deviates from the stoichiometric one toward Ti

side (Ti excessive), at a temperature lower by about 50 K than the crystallization temperature (737 K). The resulting crystals were confirmed to have formed crystal grains having a diameter of about 1 to 2  $\mu\text{m}$ . Fig. 1 is a micrograph through an ordinary electron microscope of crystal grains formed when annealing at a temperature of 687 K for two hours; and Fig. 2 is an electron micrograph showing that a crystal grain shown in Fig. 1 is composed of numerous nano-scale crystals having a diameter of 20 to 40 nm.

More specifically, Fig. 3 is a high-resolution electron micrograph of a produced nano-crystal texture when an electron beam is irradiated in the [111] bcc orientation; and Fig. 4 is an enlarged view of the box portion in Fig. 3. It is known from the images of the atomic array and lattice plane that adjacent nano-crystals are arranged in the same orientation. Further, it is also known that a small amorphous portion is existent between adjacent nano-crystals.

Fig. 5 is a high-resolution electron micrograph of a produced nano-crystal texture when an electron beam is irradiated in the [001] bcc orientation; and Fig. 6 is an enlarged view of the box portion in Fig. 5. Plate-shaped precipitate is confirmed on the boundary between adjacent nano-crystals. As can be seen in Fig. 6, the bright portion is precipitate, suggesting that this has a b.c.t. lattice, and amorphous portions are also observed on the boundaries.

Fig. 7 illustrates an atomic arrangement of a precipitate (b.c.t.) produced on a boundary between adjacent nano-crystals, which is deduced the structure images such as shown in the upper left framed region of Fig. 6; and Figs. 8 to 10 are schematic views illustrating the process of formation of nano-crystals arranged in an identical orientation.

Fig. 8 is as viewed from the [001] bcc orientation, and Fig. 9 is as viewed from the [111] bcc orientation. The shadowed portions represent precipitates. Fig. 10 three-dimensionally illustrates the whole view.

The forming process of nano-crystal will first be described for Fig.

8 having the [001] orientation. The crystallized portion (1) grows into a spherical shape. When the diameter reaches 20 to 40 nm, a plate-shaped coherent precipitate is formed on the interface with the amorphous region (shadowed portions). Then, a new crystal grain aligned coherently with the precipitate is nucleated from the interface, and grows into crystal grain (2). Subsequently, this process is repeated. A Ti-Ni alloy has a high-temperature phase of body-centered cubic lattice (b.c.c), and the plate-shaped precipitate is formed on the {100} plane. There are therefore three variants: in Fig. 8, crystal grain (2) may grow into (3). Nano-crystal grains thus three-dimensionally grow. Fig. 8 is a view projected from the [001] orientation, and Fig. 9 is a view projected from the [111] orientation.

Fig. 10 three-dimensionally represents such a nano-crystal texture as a whole: large circles are individual nano-crystal grains. For easier understanding, however, each nano-crystal grain is drawn in a form separated from the adjacent nano-crystal grains. The plate-shaped precipitate, not shown in Fig. 10, is present at a contact point of adjacent nano-crystal grains.

It is needless to mention that the present invention is not limited to the above example. Various nano-crystal textures are provided.

According to the present invention, as described above in detail, a nano-crystal texture composed of nano-crystals arranged in an identical orientation, which cannot be anticipated by conventional technology, is provided.

It is thus possible to manufacture a very tough material at a low manufacturing cost, and to incorporate properties known as a super-metal.